



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Delta/Alpha-Prime Phase Transformations in a Pu-Ga Alloy

K. J. M. Blobaum, C. R. Krenn, M. A. Wall, A. J. Schwartz

March 9, 2005

26th Compatibility, Aging, and Stockpile Stewardship
Conference
Aiken, SC, United States
April 26, 2005 through April 28, 2005

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

β/β' Phase Transformations in a Pu-Ga Alloy

Kerri J.M. Blobaum, Christopher R. Krenn, Mark A. Wall, Adam J. Schwartz
Lawrence Livermore National Laboratory, Livermore, CA

Introduction

In pure plutonium, the monoclinic β phase is the equilibrium phase at ambient temperature and pressure. The addition of a few percent of gallium, however, allows the fcc β phase to be retained metastably at ambient conditions. When the metastable β phase is cooled to subambient temperatures, it partially transforms to the monoclinic β' phase, which has gallium supersaturated in the lattice. The β' phase reverts to the β phase when the sample is heated above the ambient temperature. The martensite burst (M_b) and reversion start (R_s) temperatures are functions of the composition, heating rate, and prior thermal history. For a Pu-2.0 at% Ga alloy, the transformation hysteresis is approximately 150°C, which is large compared with other solid-solid phase transformations. Both the forward and reverse transformations are martensitic and proceed via a burst mode.¹

Here, we use differential scanning calorimetry (DSC) and resistometry to perform fundamental studies of the β/β' transformations with the goal of understanding how aging may affect β phase stability, particularly the M_b temperature. Because materials properties of the β' and β phases are considerably different (including a density increase of 25% and an accompanying resistivity increase of 46% upon transformation from β to β'), unexpected transformation to the β' phase is of particular interest to the stockpile stewardship community.

Experimental

A 2-3 year old Pu-2.0 at% Ga alloy was used for all experiments. A Perkin-Elmer Diamond differential scanning calorimeter (DSC) with liquid nitrogen cooling measured transformation temperatures and heats of transformation. DSC samples were approximately 220 mg and were hermetically encapsulated in stainless-steel pans.¹ A four-point probe (a.k.a. Kelvin probe) resistometer measured sample resistance as a function of temperature. Resistometry samples were 150 μm thick discs weighing approximately 17 mg.²

Prior to DSC and resistometry experiments, the Pu-Ga samples were annealed at 440°C for 12 hours to produce a stable distribution of single-phase β throughout the sample. In both techniques, samples were thermally cycled many times.

Results and Discussion

Burst Mode of $\beta \rightarrow \beta'$ Phase Transformations

Upon continuous cooling in a DSC or resistometer, a β -phase Pu-2.0 at% Ga alloy begins to transform to the β' phase at approximately -120°C. The transformation is observed as a gradual rise in resistance or as a smooth exothermic peak in a DSC scan. When the partially transformed sample is subjected to continuous heating, the $\beta' \rightarrow \beta$ reversion begins at approximately 32°C and is observed as a series of steps in a plot of resistance vs. temperature (Fig. 1) or as series of sharp peaks in a DSC scan (Fig. 2). When the resistometry data is differentiated with respect to temperature (Fig. 1, dR/dT), the steps appear as peaks, which are broader than the narrow, random noise spikes observed at temperatures below and above the transformation.

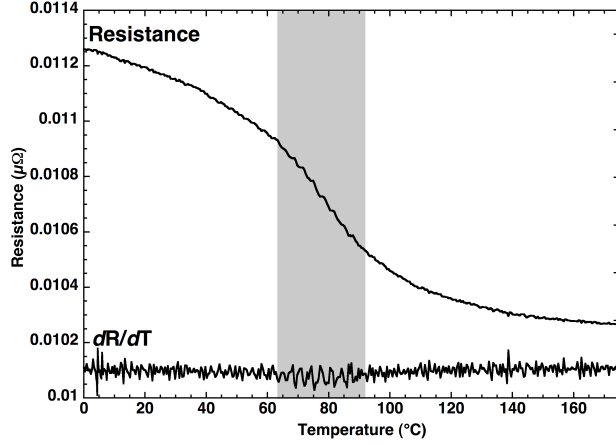


Figure 1: Resistance as a function of temperature during the $\text{BCC} \rightarrow \text{FCC}$ reversion. The heating rate was $1.5^\circ\text{C}/\text{min}$. The steps highlighted in gray, and the corresponding broad peaks in the differentiated data (bottom), result from the burst martensitic reversion of BCC' particle cascades.

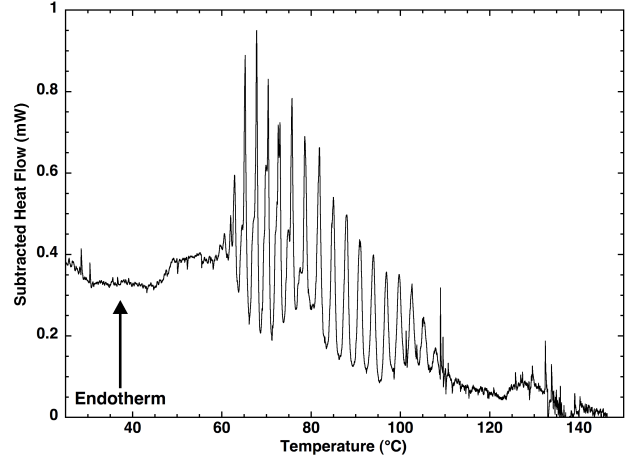


Figure 2: DSC thermogram of $\text{BCC}' \rightarrow \text{BCC}$ reversion bursts. The sharp peaks correspond to cascades of BCC' particles reverting to the BCC phase nearly simultaneously. The heating rate was $1.5^\circ\text{C}/\text{min}$.

Because the 25% volume change between the BCC' and BCC phases cannot be accommodated by purely elastic adjustments, plastic deformation must occur. Thus, the martensitic $\text{BCC} \rightarrow \text{BCC}'$ transformation and reversion proceed via the burst mode, which means that, after nucleation, particles grow to their final size at the speed of sound in the matrix.³⁻⁵ During the forward transformation, BCC' martensite particles nucleate and form as individual bursts; each of these events occurs independently as the nucleation barrier is surmounted. These individual events are too small to be detected with the techniques used here, and the resulting signals observed with these techniques correspond to the sum total of all the BCC' formation events. Thus, resistometry and DSC indicate the $\text{BCC} \rightarrow \text{BCC}'$ transformation proceeds smoothly and continuously under conditions of continuous cooling, even though each martensite particle is formed as a burst. For the reversion, however, a nucleation barrier does not exist because BCC' particles are reverted to BCC simply by moving the existing BCC'/BCC interface (the $\text{BCC} \rightarrow \text{BCC}'$ transformation is incomplete so, prior to reversion, the BCC' particles exist in a BCC matrix; during reversion, the BCC matrix simply consumes the BCC' particles). Finite-element modeling of the transformation process predicts that, after an BCC' particle reverts to the BCC phase, residual stress fields will surround the regions formerly occupied by the BCC' particles. Along the length of the reverted BCC' particle these stress fields retard further reversion, while at the particle tips, further reversion is accelerated.^{1,6} Therefore, the burst reversion of a single BCC' particle can autocatalytically trigger reversion in a cascade of additional BCC' particles. These cascades are observed as steps in resistometry plots and as sharp peaks in DSC scans. A cascade event may be quenched by the accumulation of stress in the matrix,⁷ or by temperature fluctuations caused by the reversion^{8,9} (the reversion is endothermic and may locally lower the temperature), or by a combination of these two factors.

BCC' Transformations Under Isothermal Conditions

The $\text{BCC} \rightarrow \text{BCC}'$ transformation is an isothermal martensitic transformation.^{10,11} Using continuous cooling experiments in a resistometer and a DSC, we have shown that this transformation can also occur under non-isothermal conditions, although continuous cooling can be described as a series of very short isothermal holds. In addition, we have performed long isothermal holds by

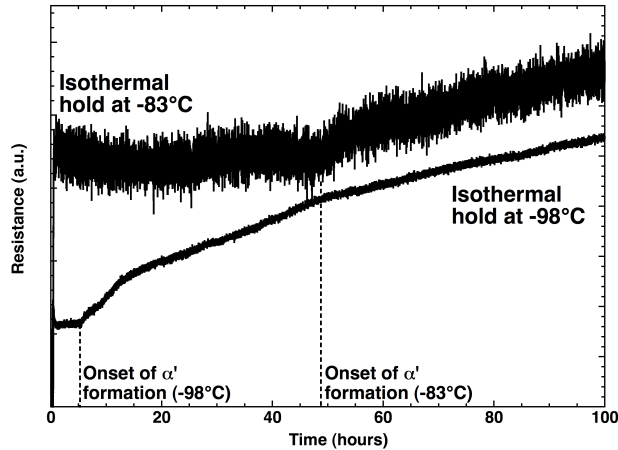


Figure 3: Resistance as a function of time for isothermal holds at -83°C and -98°C . The discontinuities correspond to the end of the incubation period and the onset of isothermal α' formation.

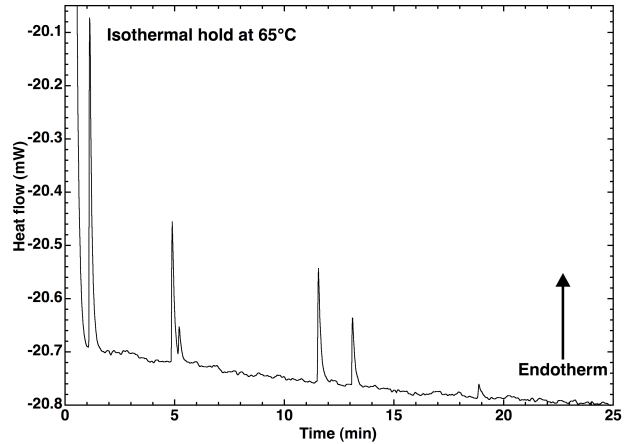


Figure 4: DSC thermogram of an isothermal hold at 65°C . Randomly spaced endothermic bursts corresponding to the $\alpha' \rightarrow \alpha$ reversion occur over 30 minutes.

quenching a sample in the resistometer and monitoring the resistance as a function of time. Plots of resistance vs. holding time at -83°C and -98°C are shown in Fig. 3. The discontinuities in the plots of resistance vs. time at 48.6 hours during the -83°C hold and 5.1 hours during the -98°C hold correspond to the onset of α' formation. The incubation periods prior to α' formation observed here are of the same order of magnitude as incubation times in the time-temperature (TTT) diagrams formulated by Orme, et al.¹² for a similar alloy.

Isothermal holds in the DSC indicate that the $\alpha' \rightarrow \alpha$ reversion can also occur isothermally. Furthermore, the isothermal reversion occurs in autocatalytic cascades via the burst mode, as was observed in the continuous cooling experiments. Fig. 4 is a DSC thermogram of an isothermal hold at 65°C . Prior to the hold, the sample was cooled to subambient temperatures to form α' . During the isothermal hold, a large initial burst and a series of successively smaller bursts were observed over the course of 30 minutes, and the time interval between successive bursts is not constant. Similar isothermal work with a burst martensitic steel demonstrated that changes in temperature induce additional transformation bursts.

Nucleation of the α Phase at Room Temperature

A single Pu-Ga sample can be thermally cycled many times, with the same amount of α' formed and reverted during each cycle, provided an appropriate annealing sequence is performed after each cycle. Specifically, the sample must be annealed at 375°C for 8 hours and then conditioned at 25°C for at least 6 hours. This ambient temperature conditioning step is crucial! The possible events occurring during this conditioning period were thoroughly investigated with a series of DSC scans in which both the conditioning time and temperature were varied before the samples were thermally cycled. The amount of α' formed upon continuous cooling was estimated from the integrated area of the $\alpha' \rightarrow \alpha$ reversion peak because integration of this heating peak yields more consistent results. (Note that the sharp peaks corresponding to the reversion described earlier in DSC scans at $1.5^{\circ}\text{C}/\text{min}$ are not apparent at the $20^{\circ}\text{C}/\text{min}$ cooling and heating rates used in these experiments.¹) In Fig. 5, which shows the reversion peaks observed after a series of 0 to 12 hour conditioning treatments at 25°C , the amount of reversion increases as the conditioning time is increased from 0 to 6 hours, but longer times do not

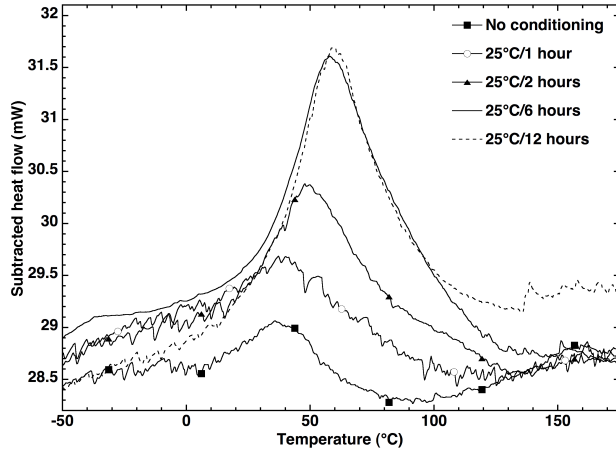


Figure 5: DSC peaks corresponding to the $\alpha' \rightarrow \alpha$ reversion at a heating rate of 20°C/min following conditioning treatments at 25°C for various times. The largest amount of reversion is observed when the conditioning time is at least 6 hours. Conditioning treatments longer than 6 hours at 25°C do not result in more reversion.

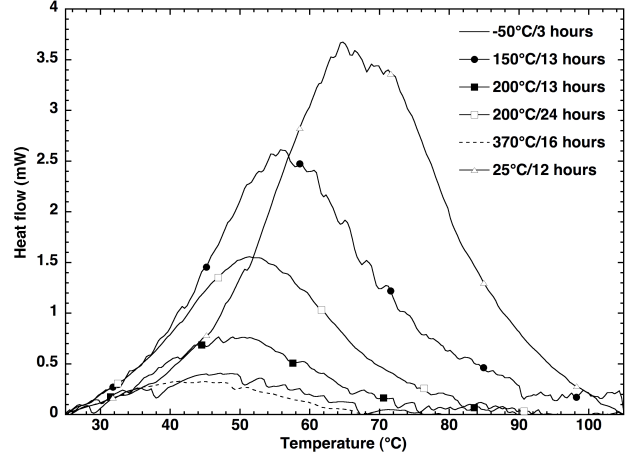


Figure 6: DSC peaks corresponding to the $\alpha' \rightarrow \alpha$ reversion at a heating rate of 20°C/min following conditioning treatments at various temperatures. Conditioning treatments at 25°C result in the largest amount of reversion.

generate additional reversion. Fig. 6 shows reversion peaks formed after a series of conditioning treatments at temperatures ranging from -50°C to 370°C . The largest reversion peak occurs when the conditioning temperature is 25°C ; neither higher temperatures (up to 370°C) nor a lower temperature (-50°C) result in a larger amount of α' reversion. In fact, 370°C and -50°C conditioning treatments result in approximately the same amount of reversion as is observed in thermal cycles performed without a prior conditioning treatment.

Ultimately, the amount of α' formed (and reverted) is probably limited by matrix strain. These experiments, however, suggest that an ambient temperature process on the order of many hours is also essential for maximizing α' formation. At 25°C , $\alpha + \text{Pu}_3\text{Ga}$ are the expected phases for a Pu-2.0 at% Ga alloy, according to the Russian equilibrium phase diagram.^{13,14} Although complete eutectoid decomposition is expected to take on the order of 10,000 years,¹⁴ embryos of α and/or Pu_3Ga may form on a short time scale. These embryos may serve as nucleation sites for α' when a sample is later cooled. It is likely that α embryos could form slightly off-composition, and since they have the same crystal structure as α' , they would more readily nucleate α' than embryos of Pu_3Ga . Thus, we believe the conditioning treatment allows α embryos to form, and these embryos facilitate α' formation upon subsequent cooling. If this explanation of the necessity of the conditioning treatment is correct, it is an indirect confirmation of the Russian phase diagram. How or if this process may change with age is still an open question.

Conclusions and Future Work

Investigations of the α'/α phase transformations in Pu-Ga alloys are currently underway at Lawrence Livermore National Laboratory. With a solid scientific understanding of the underlying mechanisms responsible for these phase transformations, we expect to improve our ability to predict how aging affects stability of the α phase in Pu-Ga alloys.

Both the $\alpha \rightarrow \alpha'$ transformation and the $\alpha' \rightarrow \alpha$ reversion can occur under conditions of continuous thermal cycling or isothermal holding. Before the $\alpha \rightarrow \alpha'$ transformation can be initiated at subambient temperatures, the sample must be conditioned at 25°C for several hours.

During this time, it is believed that embryos of the β phase form and these β embryos provide nucleation sites for β' upon subsequent cooling. Both the forward and reverse phase transformations proceed via a burst martensite mode, with the reversion occurring in autocatalytic cascades that are quenched by stress and/or temperature fluctuations, both of which can be produced by the transformation itself.

In the upcoming months, transformations in an old Pu-Ga alloy will be investigated with differential scanning calorimetry. Initial experiments will determine if the M_b and R_s temperatures change with age. Additional experiments will be undertaken to study how β' formation and reversion may be affected by aging. Specifically, we hope to answer a series of questions: Does the incubation period for β' formation at subambient isothermal holds change with age? Could isothermal transformation to β' occur at ambient conditions over very long times? How does β' microstructure vary with age and formation conditions? Is the autocatalytic burst reversion influenced by age? The fundamental scientific research into β/β' transformation mechanics and kinetics described here provides a foundation for thoroughly understanding β phase stability, which is essential for developing models to predict aging effects in Pu-Ga alloys.

Acknowledgements

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

References

1. K. J. M. Blobaum, C. R. Krenn, J. N. Mitchell, J. J. Haslam, M. A. Wall, T. B. Massalski, and A. J. Schwartz: submitted to *Metall. Mater. Trans. A*, 2005.
2. J. J. Haslam, M. A. Wall, D. L. Johnson, D. J. Mayhall, and A. J. Schwartz: in *Electrically Based Microstructural Characterization III*, edited by R. A. Gerhardt, A. P. Washabaugh, M. A. Alim, and G. M. Choi, Mater. Res. Soc. Symp. Proc., vol. 699, Pittsburgh, PA, 2002, pp. 295-300.
3. R. F. Bunshah and R. F. Mehl: *T. Am. I. Min. Met. Eng.*, 1953, pp. 1251-1258.
4. R. E. Cech and J. H. Hollomon: *T. Metall. Soc. AIME*, 1953, vol. 197, pp. 685-689.
5. C. R. Heiple and S. H. Carpenter: *J. Nucl. Mater.*, 1987, vol. 149, pp. 168-179.
6. K. J. M. Blobaum, C. R. Krenn, J. J. Haslam, M. A. Wall, and A. J. Schwartz: in *Actinides--Basic Science, Applications, and Technology*, edited by L. Soderholm, J. J. Joyce, M. F. Nicol, D. K. Shuh, and J. G. Tobin, Mater. Res. Soc. Symp. Proc., vol. 802, Pittsburgh, PA, 2003, pp. 33-38.
7. R. E. Cech and D. Turnbull: *T. Am. I. Min. Met. Eng.*, 1956, vol. 206, pp. 124-132.
8. R. Brook and A. R. Entwisle: *J. Iron Steel I.*, 1965, vol. 203, pp. 905-912.
9. V. Raghavan: in *Martensite: A Tribute to Morris Cohen*, edited by G. B. Olson and W. S. Owen, ASM International, Materials Park, OH, 1992, pp. 197-225.
10. C. R. Heiple and S. H. Carpenter: *Metall. Trans. A*, 1992, vol. 23A, pp. 779-783.
11. S. S. Hecker: *Los Alamos Science*, 2000, vol. 26, pp. 290-335.
12. J. T. Orme, M. E. Faiers, and B. J. Ward: in *Plutonium 1975 and Other Actinides*, edited by H. Blank and R. Lindner, North-Holland Publishing Company, Amsterdam, 1975, pp. 761-773.
13. N. T. Chebotarev, E. S. Smotriskaya, M. A. Andrianov, and O. E. Kostyuk: in *Plutonium 1975 and Other Actinides*, edited by H. Blank and R. Lindner, North Holland Publishing Co., Amsterdam, 1975, pp. 37-46.
14. S. S. Hecker and L. F. Timofeeva: *Los Alamos Science*, 2000, vol. 26, pp. 244-251.